

DESCRIPTION

"METHOD FOR THE MODIFICATION OF POLYACRYLONITRILE FIBRES
5 CONTAINING VINYL ACETATE AS A COMONOMER AND POLYAMIDE
FIBRES, USING A CUTINASE ENZYME"

Field of the invention

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The quality and the processing properties of filaments in the extrusion line, fibres, yarns and textile fabrics can be improved by modifying their surface. The traditional processes used for their modification require 15 chemical agents with negative environmental effects. These negative effects can be prevented by using new processing techniques based on biotechnology.

Enzymatic processes can be used to modify the 20 surface of fabrics constituted by synthetic fibres. Hydrolysis of polyacrylonitrile fibres containing vinyl acetate as a comonomer and polyamide fibres results in the formation of hydrophilic groups. The increase in these groups at the surface of the fibres provides hydrophilic 25 characteristics, therefore improving the comfort properties. This treatment also allows these fibres to be dyed with specific reactive dyes.

Background of the invention

Cutinase 3.1.1.74 is an esterase which degrades cutine, a structural polymeric component of plants composed of fatty acids (Carvalho et al., *Biotech. Bioeng.*, 1999, 66, 17-34). This is an enzyme which is not very specific and which hydrolyses soluble and non-soluble p-nitrophenyl esters and triglycerides.

Several patents exist relating to the genetic enhancement of *Fusarium solani* cutinases and their application in the formulation of detergents for washing machines and dishwashers. These products have shown better lipolytic action than other products previously used (IN183592, EP1290150, AU1503800, AU5488090, US5512203, WO9414964, GB2296011, WO8809367, EP0399681). In the textile field, the use of cutinases to reduce backstaining during stone-wash processes in cotton denim fabrics is also described (CA2413838, US2002066144). Cutinase is also described as being able to degrade aliphatic and aromatic polyesters (US6255451).

Cutinase is an esterase which shares the catalytic triad of serine-histidine-aspartic acid with other esterases and amidases, meaning that the degradation of amides besides ester groups is theoretically possible. Recent research demonstrates that cutinase has activity in more hydrophobic media due to the external amino acids in the 3D structure (Vidinha et al. (2003) "Effect of immobilization support, water activity and enzyme

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ionization state on cutinase activity and enantioselectivity in organic media", Biotechn. Bioeng., accepted).

5 The chemical agents of fibre modification described in general do not restrict their action to the fibre surface, rather they also penetrate inside and degrade the fibres with deterioration of their properties. One of the treatments that was normally carried out to
10 improve touch and increase the hydrophilicity of synthetic fibres was alkaline treatment with high concentrations of caustic soda. These treatments were damaging, not only to the physical performance of the fibres but also to the environment where the residues of this product were
15 deposited (US20030119172).

Several chemical methods have been used in order to improve the structure of polyamide fibre. The modification of this fibre, according to the method
20 described in the patent GB1072070, is carried out by acylation of the peptidic groups as well as of the terminal amino groups of the polyamide for greater polyamide reactivity. Another method already described in the patent US5599698 specifies the treatment of polyacrylonitrile
25 fibre containing vinyl acetate as a comonomer with a nitryl hydratase enzyme, in order to modify its hydrophilicity and consequently its comfort properties, also allowing the polyacrylonitrile fibres containing vinyl acetate as a comonomer to be dyed with acid dyes.

Detailed Description of the Invention

This invention describes the use of cutinase to modify the surface of synthetic polyacrylonitrile fibres containing vinyl acetate as a comonomer and polyamide fibres. Superficial hydrolysis of the ester and amide groups of the polyacrylonitrile fibres containing vinyl acetate as a comonomer and polyamide fibres, respectively, causes the formation of hydroxyl groups in the polyacrylonitrile fibres containing vinyl acetate as a comonomer and carboxylic and amino groups in the polyamide fibres. The increase in these groups at the surface of the fibres gives the fabric hydrophilic characteristics, therefore improving the comfort properties. This treatment also allows the polyacrylonitrile fibre containing vinyl acetate as a comonomer to be dyed with reactive dyes (used for cotton) and the polyamide fibre to be dyed with reactive dyes (used for wool). To date, no method for the modification of the vinyl acetate comonomer of acrylic or polyamide has been described in scientific literature or patents.

A first embodiment of the invention consists of a method for the treatment of polyacrylonitrile fibre containing vinyl acetate as a comonomer, which comprises the contact of the fibre with an enzyme solution in order to modify the chemical surface of the fibre, increasing the number of hydrophilic hydroxyl groups.

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A second embodiment of the invention consists of a method for the treatment of polyamide fibre, which comprises the contact of the fibre with an enzyme solution in order to modify the chemical surface of the fibre,
5 increasing the number of hydrophilic amino groups.

The treatment of the polyacrylonitrile fibre containing vinyl acetate as a comonomer or the polyamide fibre is preferably carried out using an enzyme with
10 esterase action.

The enzyme preferably contains the catalytic triad of serine-histidine-aspartic acid.

15 The abovementioned enzyme esterase is preferably a hydrolase that degrades cutine.

The amount of enzyme used is normally between 1 and 400 g of protein per kg of fibre.

20 In both of the embodiments described above, a treatment bath with a retrievable and reusable enzyme is used.

25 **Examples**

The method consists of the chemical modification of the surface of polyacrylonitrile fibres containing vinyl acetate as a comonomer (constituted by about 93%

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acrylonitrile and 7% vinyl acetate) and polyamide fibres through the action of a cutinase solution obtained from the heterologous expression of *Fusarium solani pisi* cutinase, by the *Escherichia coli* DHB4 transformed strain.

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The treatment was carried out in a ROTAWASH machine that simulates dyeings and other textile treatments. Each container had between 1 and 2U ($\mu\text{mol}/\text{min}$ as pNPP - paranitrophenolpalmitate) of cutinase activity.

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Example 1:

Enzymatic modification of polyacrylonitrile fibre
containing vinyl acetate as a comonomer

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Samples of 0.7 g of polyacrylonitrile fabric containing vinyl acetate as a comonomer were washed with water containing 1 g/L of Lutensol and dried at 50°C. The samples were then placed in a container with 1 U of 20 cutinase, in a bath ratio of 1:35 (p/v). The treatment was carried out at pH 7.5 and at 30°C, for a period of 700 hours. The samples were removed from the solution, washed with water containing 2 g/L of Na₂CO₃ and dried at room temperature.

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Hydrolysis was confirmed by the formation of acetic acid and the dyeing of the treated samples. No acetic acid was detected in the treatment baths. The samples were dyed with 2% reactive dye Remazol Brilliant

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Blue, using a bath ratio of 1:50 (p/v), at 70°C. In the samples treated for 700 hours with the enzymatic solution of cutinase, the value of K/S (spectral coefficient) increased by an average of 30% in relation to the non-
5. treated sample.

Example 2:

Enzymatic modification of polyamide fibre

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Similar treatments were carried out to polyamide fabric using the following parameters: fabric samples of 1 g were washed with water containing 1 g/L of Lutensol and dried at 40°C. They were then placed in a specific
15 container in the ROTAWASH machine with 2 U of cutinase, in a bath ratio of 1:200 (p/v). The treatment was carried out at pH 8.5 at 30°C, for a period of 97 hours. The samples were removed from the solution, washed with water containing 2 g/L of Na₂CO₃ and dried at 40°C. The
20 hydrolysis that occurred in the samples treated with the enzymatic solution was verified through dyeing with a reactive dye. The samples treated for 97 hours were dyed with 2% reactive dye (Lanasol Red 66), obtained from CIBA, using a bath ratio of 1:100, at 60 °C. In the samples
25 treated, the value of K/S (spectral coefficient) increased in relation to the non-treated sample by 11.67% (60°C).